

CATTLEHIDE PRESERVATION WITH SODIUM SULFITE AND ACETIC ACID*

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ABSTRACT

A practical nonsalt method of cattlehide preservation is needed to reduce the dissolved solids content of tannery effluents. A method has been developed which utilizes a combination of sodium sulfite and acetic acid as a replacement for salt curing. This treatment has been tested on whole hides with excellent results under several different industrial conditions. The results demonstrate that the sulfite/acetic acid preservation can be used for short term preservation, either for direct processing or as a holding treatment prior to brine curing. Its full potential as a long-term preservation method remains to be tested.

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INTRODUCTION

The need for a nonsalt preservation of cattlehides has been firmly established. Pollution control regulations around the world, as well as effluent treatment methods, recognize the need to lower the soluble solids content of tannery and packinghouse effluents. Standards have already been set in South Africa, and Dr. Stanley Shuttleworth in his 1973 John Arthur Wilson Memorial Lecture to the ALCA suggested that elimination of salt in hide preservation is the only way these standards can be met. Soluble solids in tannery effluents remain the most difficult and expensive pollution problem to treat. The best solution is not to add them in the first place.

Various nonsalt methods of preservation have been proposed. These include the nonaqueous solvent dehydration processes (1), and treatments with chlorite and sodium pentachlorophenate (2), benzalkonium chloride (3), or zinc chloride and sodium pentachlorophenate (4). A number of commercial materials are available which are claimed to provide a temporary hide preservation. Each method has potential as well as limitations.

Any material or process that replaces salt must conform to many of the conditions met by salt. It must be reliable and rapidly bring the fresh hide to a stable condition. It should be low in cost, nonpolluting, and relatively easy to apply.

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Most of all, it must not have an adverse effect on the quality of leather produced from the preserved hides. The preservation treatment developed in our laboratory, utilizing sodium sulfite[‡] and acetic acid, appears to fit these criteria.

Sulfite, the effective material in this preservation method, is an industrial chemical commonly used for its antioxidant and antimicrobial action. Large quantities are used in the manufacture of paper and maraschino cherries and in the bottling of wine (5). In an aqueous solution, at low pH, sulfite exists as dissolved sulfur dioxide gas. As the pH increases, an equilibrium is established between the gas and bisulfite ions, and, at higher pH, with sulfite ions (Figure 1).

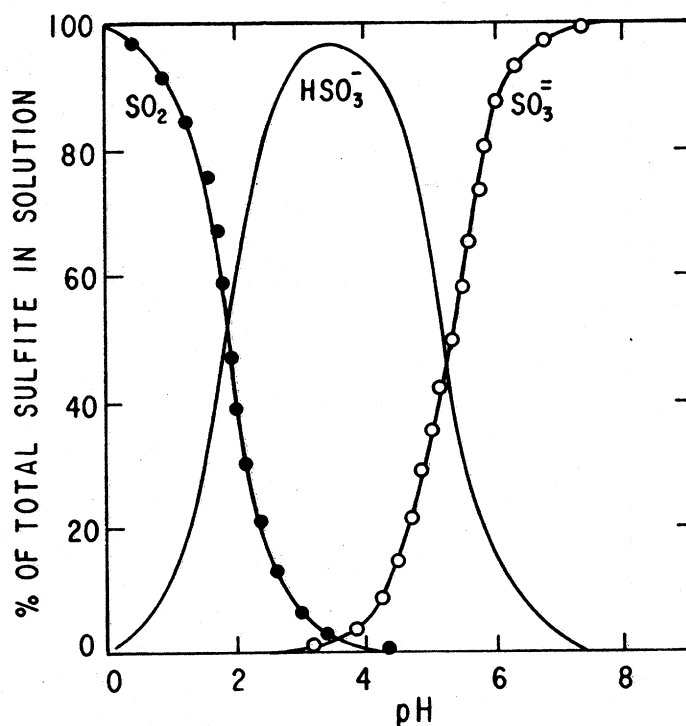


FIGURE 1.—Effect of pH on HSO_3^- , $\text{SO}_3^{=}$, SO_2 equilibrium.

Antimicrobial activity is associated with the sulfur dioxide (6). For the maintenance of an effective preservation system, the pH must be kept low enough so that a small amount of sulfur dioxide is present, but not so low that a large percentage of it is lost as a gas or oxidized to sulfate ions.

The preservative effect of acetic acid and sulfite on cattlehides was originally reported by Hopkins *et al.* (7) and has been discussed in a series of papers and

[‡]Caution must be exercised with acid solutions containing Na_2SO_3 because of SO_2 evolution.

presentations concerning the process (8-10). We tested the efficacy of sulfite/acetic acid preservation in four multi-side experiments carried out in three industrial locations, primarily by tannery personnel.

RESULTS AND DISCUSSION

The objective of the first test was to determine the effect of a seven-day sulfite/acetic acid preservation on shoe upper leather. At the S. B. Foot Tannery** in Red Wing, Minnesota, twenty-five hides were sided, and alternating right and left sides were brined as experimental controls. The corresponding opposite sides were placed in an experimental drum along with acetic acid and sodium sulfite, each in an amount equal to one percent of the weight of the sides. The acid and sulfite were dissolved in a twenty-percent float before being added to the drum. The sides were then drummed continuously for one hour. The wet sides were placed in plastic-lined fiber drums and held at room temperature for a week.

At the end of the storage period the sides were processed into crust shoe upper leather and evaluated by tannery personnel. Physical testing was performed at the Eastern Regional Research Center. The results demonstrated that the sulfite/acetic acid treatment had no adverse effect on the final leather quality. The only differences noted were that the color of the test leather was lighter than the salt control, and the sulfite preserved sides had less draw. Physical test data on SATRA and tensile strength showed no statistically significant differences (10). The sides held for a week by this procedure were converted into shoe upper leather of at least equal quality to the brined controls.

A larger scale test of the sulfite preservation method was conducted by the Tennessee Tanning Company. Two hundred and fifty hides were treated in a concrete mixer with one percent acetic acid and one percent sodium sulfite in a 25-percent float. After treatment for two hours, they were spilled out into slat boxes lined with polyethylene sheets and shipped to Colquitt Tanning, where they were fleshed and repacked. After being held for one week at room temperature, they were processed into baseball glove and softball leather. These results also confirmed that the hides were preserved as well as those in normal production.

The second type of industrial test was performed to determine if an easily applied short-term cure would enable hides to be preserved for several days during hot weather prior to brine curing. The experiment was conducted at John Wake's Locker Plant in Wyoming, Illinois, during the months of July and August. One day a week, hides were removed from the kill floor and placed in a plastic barrel containing a premixed solution of acetic acid and sodium sulfite. The hides were held in a metal shed until picked up one week later. Control

**Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

hides were taken to be brined the day after slaughter without further treatment. They were taken to a central brine-curing facility operated by National By-Products, Inc., in Galesburg, Illinois, and placed in a brine raceway for 18 hours. This procedure was repeated eight times and a total of 100 sides (56 control and 44 experimental) was accumulated. At the end of this phase, the sides were marked and transported to Seidel Tannery in Milwaukee, where they were manufactured into crust shoe lining leather. Physical tests and general quality evaluations were made at ERRC, and a final quality sort was also done in the same manner as in the normal production. It was observed that the amount of draw visible in the sulfite treated sides was considerably less than the draw present in the untreated sides. Physical test data showed a significant difference in tensile strength between the treated (average 2,024 p.s.i.) and untreated (average 1,569 p.s.i.) leather. The sides were graded into #1, #2, and #3 quality crust stock. The distribution of grades was very similar for hides held for one week in the preservative solution and for the hides placed directly into the brine cure (Table I).

TABLE I
RESULT OF QUALITY EVALUATION FOR
CRUST SHOE LINING LEATHER

Grade	Control		8-Day Sulfite	
	No.*	%**	No.*	%**
#1	31	58	9	50
#2	11	21	5	28
#3	9	17	3	17
Reject	2		1	

*Number of hides.

**Percent of total hides in the set.

A third type of test was carried out in co-operation with Transcontinental Leathers, Inc., to determine the effect of longer storage on sulfite-treated hides to be manufactured into garment leather. Good quality garment leather was prepared after a 30-day preservation at room temperature. Unfleshed, undressed, unwashed hides were used as raw material. The hides were drum treated for an hour in a 20-percent float containing one percent sodium sulfite and one percent acetic acid based on hide weight, and then stored individually in plastic bags and held for 30 days. These hides were processed along with fresh hides. The resulting leather was similar in physical properties and judged to be soft and supple, and equal to or better than that in normal production.

Disposal of the fleshings from hides treated with the sulfite and acetic acid was discussed with a renderer. Although no experimental work was done, he felt

confident that neither of these materials, acetic acid or sodium sulfite, would have a detrimental effect on his rendering process.

Each preservation test on whole hides considered so far has been done for relatively short periods of time. To have an impact on international trade, the duration of preservation must be greater than the 30 days we have tested.

The original screening process used to find potential materials to preserve hides was performed using 100-gram pieces of hide. The criterion used to evaluate preservation was whether the bacterial growth on the hide piece was retarded or eliminated by the treatment. Promising treatments were then tested on full hides for their effect on leather manufacture. On the basis of elimination of bacterial growth alone, the sulfite and acetic acid does have potential for long-term preservation (Table II). Hide pieces have been held for over a year with little or no bacterial growth. It is not presently known whether this process can provide a similar long-term preservation on full hides with retention of leather-making properties.

TABLE II
PRESERVATION OF EXPERIMENTAL
HIDE PIECES* BY SOLID SODIUM BISULFITE (2%)

	Preservation time (days)	Bacteria/gram of hide
Fleshed hides*	14	<1,000
"	35	<1,000
"	52	<2,000
"	365	††
Unfleshed hides†	7	450,000
"	11	9,000
"	87	11,000

*Samples cut from fleshed and demanured hides that were frozen until treatment with preservative.

†Samples cut from fresh hides that were not fleshed or demanured.

††Good by observation and odor.

CONCLUSION

Our work to date has shown that sulfite and acetic acid have a great deal of potential as a nonsalt method of preservation of cattlehides. It is currently being tested for use by companies in Canada and the United States, in addition to those tests being done in co-operation with the Department of Agriculture. Economic considerations appear to be favorable, with the cost varying with the location, but, in general, being less than salt. It is rapid, and soaking is not necessary at the tannery, since the hides remain in a flaccid condition after treat-

ment. Reliability and easy application for the short cure have been demonstrated. Its potential for long-term preservation and, therefore, its potential as a full replacement for salt curing remains to be established.

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